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WATER QUALITY BASIC DATA. REPORT ON ANALYTICAL REFERENCE SAMPLE TYPE II, BD-1

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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water quality basic data

report on analytical reference sample

TYPE II, BD-1

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Public Health Service

ROBERT A. TAFT
SANITARY ENGINEERING CENTER

Cincinnati, Ohio

Participants in the Study of Reference
Sample, Type II, BD-1 (Distributed February 12, 1959)

Yankton Water Department
Yankton, South Dakota

East St. Louis Water Co.
East St. Louis, Illinois

Cairo Water Company
Cairo, Illinois

City Water Department
Cincinnati, Ohio

Board of Water Commissioners
Water Works Park Filtration Plant
Detroit, Michigan

Chemical-Toxicological Laboratory
Louisiana State Health Dept.
New Orleans, Louisiana

Metropolitan Utilities District
Omaha, Nebraska

Corps of Engineers
Dalecarlia Filtration Plant
Washington, D. C.

Massachusetts State Dept. of Health
Lawrence Experiment Station
Lawrence, Massachusetts

Crown Zellerbach Corporation
Central Research Dept.
Camas, Washington

Erie County Dept. of Health
Buffalo, New York

Evansville Water Dept.
Evansville, Indiana

Minneapolis-St. Paul Sanitary
District
St. Paul, Minnesota

Dubuque Water Department
Dubuque, Iowa

City of Memphis
Light, Gas & Water Div.
Memphis, Tennessee

St. Joseph Water Company
St. Joseph, Missouri

Hagerstown Water Department
Hagerstown, Maryland

Board of Public Utilities
Kansas City, Kansas

Water, Gas & Sewage Treatment Dept.
Duluth, Minnesota

City of St. Louis Water Dept.
St. Louis, Missouri

St. Louis County Water Company
University City, Missouri

Mississippi State Board of Health
Chemical Laboratory
Jackson, Mississippi

Weiser Water Department
Weiser, Idaho

N. Dakota State Dept. of Health
Public Health Laboratory
Bismarck, North Dakota

INTRODUCTION

Much of the physical and chemical data reported by the Public Health Service National Water Quality Network in its annual compilation of water quality data are the result of the cooperative efforts of laboratories located at or near the sampling sites. Because these analyses originate from different sources, it is necessary that they be comparable as to accuracy. The reference sample technique is the mechanism by which this objective is being attained. Reference samples are submitted periodically to each cooperating laboratory to insure the accuracy of the data reported. The results of the reference samples are useful in judging the quality of data previously submitted by cooperating laboratories and also serve to alert the laboratories to possible errors in method or technique that may pass undetected in normal laboratory operations.

REPORT ON THE ANALYTICAL REFERENCE SAMPLES TYPE II, BD-1

This Type II reference sample is our first attempt to evaluate the procedures and techniques involved in the determination of the "demand" type analyses so important to water quality evaluation. Because it is practically impossible to provide standard samples for the direct determination of these parameters, due to changes which occur with time, our approach to this problem was an indirect one. By preparing standard solutions, which when added to raw samples produce measurable and precise effects on the samples, we hoped to discover errors in technique, procedure, or other factors which affect these tests and thus alert the cooperating laboratories and to the program to possible sources of error.

The standard solutions were so prepared that when a specified quantity was added to a duplicate sample to be analysed, the difference between it and the original sample would be a precise quantity. Deviations from the expected difference would thus serve to indicate the proficiency of the laboratory performing the analysis. Judging from the results of this reference sample, we feel that this technique was successful in that many of the laboratories were able to carry out the exercises successfully and with others it pointed out the areas in which they may need further assistance.

This sample was sent to 35 laboratories in the Network which contribute data on one or more of the tests being evaluated. Twenty-four reported their results in time to be included in this report. Except for B.O.D. most of the results were within the expected accuracy of the tests being reported. Undoubtedly, some of the low B.O.D. results were influenced by the lack of active biological forms (seed) and lack of nutrients, (nitrogen and phosphorous) in the raw waters at several of the Network stations. In the absence of a balanced biological environment or a shortage of elements necessary for optimum biological growth the B.O.D. reaction will not proceed at its normal rate, giving low results. Therefore, in evaluating laboratory performance these factors should be kept in mind. This is particularly true with laboratories 8, 17, and 20, where the raw waters are known to be deficient in the ingredients necessary for the optimum B.O.D. reaction rate.

The individual analyses are presented in the tables and bar graphs appended to this report. We strongly urge all cooperating laboratories to study their performance against the expected accuracy for the various tests and to communicate with us regarding any questions they may have as to the procedures and techniques involved.

DISCUSSION OF RESULTS

Statistical comparisons in this report were developed from the deviations from known quantities added to the sample. The range of deviations considered acceptable to the program were based on the precision and accuracy values as presented in "Standard Methods" for the various tests involved. Table I, below, is a summary of the expected accuracy for the various tests from "Standard Methods" and the ranges acceptable to the Water Quality Network for this reference sample.

Laboratories reporting values outside the range of acceptability should investigate their procedures for sources of error. Have standard solutions been properly prepared and checked? Are sample sizes adequate for maximum accuracy? Is pipetting technique correct? A thorough review of the details in each procedure may disclose errors which have become habitual and escape unnoticed during routine operations.

TABLE I

ACCEPTABLE LIMITS OF ACCURACY

	Standard Methods	Water Quality Program
Dissolved Oxygen	± 0.1 mg/l	± 0.2 mg/l
Biochemical Oxygen Demand	± 0.11 mg/l	± 0.33 mg/l
Chemical Oxygen Demand	± 1.6 mg/l	± 3.2 mg/l
Ammonia Nitrogen (direct Nessler)	± 0.1 mg/l	± 0.1 mg/l

The Tenth Edition of "Standard Methods" gives the expected precision and accuracy for each test, within the range of concentration normally encountered in water analysis. These "standards of accuracy" should be attainable by most laboratories performing these routine examinations. The additional errors, allowable for the Network Program, are intended only as a guide to the cooperating laboratories and are not to be considered as the ultimate goal in the achievement of laboratory accuracy. The principal reason for the additional allowance is that each determination in this sample involved a double analysis, one on raw water and one on river water plus sample, thus compounding the possible error. The B.O.D. error allowance is increased an additional 0.11 because of the inherent error in the B.O.D. of the standard used.

DISSOLVED OXYGEN - 1.5 mg/l

Because the preparation of a stable reference sample containing a known quantity of dissolved oxygen is impractical, this test was evaluated by using a reagent which would produce a calculated reduction in D.O. when added to a duplicate sample. The analyst collected duplicate samples of river water by the proper D.O. technique. He determined the D.O. on one of the samples and repeated the analysis after adding a prescribed quantity of the reference solution to the second bottle. The decrease in D.O., if the test was performed properly, should be 1.5 mg/l ± 0.2.

Of the 23 laboratories reporting this analysis, 16 submitted results within acceptable limits. Possible reasons for the gross errors reported by several laboratories may be improper sampling, improper introduction of the reference sample into the D.O. bottle, too much delay between analyses, permitting the second portion of water to warm up, thereby reducing the dissolved oxygen level, and improperly standardized reagents.

BIOCHEMICAL OXYGEN DEMAND - 2.24 mg/l

In this test we collected a large sample of river water and divided into two parts. The first portion was handled in routine fashion. Two or more bottles were filled, using the proper technique; one of these was analysed for initial D.O. and the remainder incubated for 5 days. To the second portion was added a calculated quantity of reference solution. Two or more bottles were filled using the proper technique; one of these was analysed for initial D.O., and the remainder incubated concurrently with the first series. After the 5 day D.O. was determined for the incubated samples, the B.O.D. for each series was calculated. The series containing the reference sample should result in an increased B.O.D. of 2.24 mg/l ± 0.33.

Of the 21 laboratories reporting this analyses only 9 fell within the acceptable limits of accuracy. This was somewhat disappointing but may be partially due to lack of proper seed and nutrients present in the raw waters available to some of these laboratories, as was discussed in the opening paragraphs. In several instances, the errors may have been due to failure of the analyst to reduce the initial D.O. of the sample to its saturation limit of 9.2 mg/l at 20°C, the temperature of incubation. This was especially true of laboratories 14, 15 and 23 as noted on the reports submitted. Other errors may be due to improper mixing of samples, entrainment of air, incorrect incubation temperature or improperly standardized reagents.

CHEMICAL OXYGEN DEMAND - 21.3 mg/l

In this examination the analyst performed the C.O.D. determination on a sample of raw water and on a duplicate to which had been added a specified quantity of the reference solution. The C.O.D. was calculated for the two determinations, and the increase in C.O.D. of the second determination recorded. The increase in C.O.D., if the procedure was carried out properly, should be 21.3 mg/l ± 3.2. Of the 19 laboratories reporting this test 11 fell within the acceptable limits and 2 others were barely outside the limits. Factors which could contribute errors to this test are improperly standardized reagents and the cleanliness of glassware used in the digestion. The latter may be particularly significant in this exercise since most of the laboratories outside the acceptable range reported low results. Contamination in the digestion apparatus would produce a high result in the initial

C.O.D. which would then calculate out as a low result in the final calculation since the contamination would not be present in the second digestion, if performed immediately following the first one.

Contaminated glassware is one of the most serious problems in the accurate determination of low C.O.D, values. Because the oxidation is carried out using diluted reagents, small amounts of extraneous material, not part of the sample, produce large errors in the ultimate result and cannot be compensated by "blank" runs. Therefore, every effort should be made to maintain the digestion apparatus and other equipment "chemically clean" in order to achieve ultimate accuracy in this test.

Laboratory 16 determined the C.O.D. by the Permangonate method, which is no longer considered standard. The low results obtained show the incomplete oxidation resulting from the use of this method.

AMMONIA NITROGEN - 0.4 mg/l

This test is similar to the others in that the raw sample is analysed for ammonia both before and after the addition of a standard ammonia solution. The difference between the two readings should be 0.4 mg/l ± 0.1. The results of this determination were very good with only four of the 19 laboratories falling outside the acceptable range. Those outside the range were on the low side. These low values may be the result of weak Nessler reagent, improper standards or arithmetic errors. Cloudiness in the sample following addition of Nessler reagent was noted by some of the laboratories. This can usually be eliminated by carrying out the zinc sulfate pre-treatment and also by addition of Rochelle salt as specified in the procedure.

PART I

DISSOLVED OXYGEN

Lab #	River Water D.O. mg/l	R.W. & Sample A D.O. mg/l	Diff. Due to Sample A mg/l	Deviation mg/l
Theoretical			1.5	± 0.2
*SEC	11.45	9.97	1.5	0
1	12.58	10.71	1.9	+ 0.4
2	10.27	8.79	1.5	0
3	10.5	9.1	1.4	- 0.1
4	8.8	7.6	1.2	- 0.3
5	7.2	6.0	1.2	- 0.3
6	10.00	8.50	1.5	0
7	8.12	6.73	1.4	- 0.1
8	14.75	13.12	1.6	+ 0.1
9	10.3	9.1	1.2	- 0.3
10	11.5	10.0	1.5	0
11	10.23	9.40	0.8	- 0.7
12	-	-	-	-
13	11.1	9.2	1.9	+ 0.4
14	14.0	12.6	1.4	- 0.1
15	8.40	6.93	1.5	0
16	10.9	9.1	1.8	+ 0.3
17	13.2	11.9	1.3	- 0.2
18	12.15	10.65	1.5	0
19	8.47	7.13	1.3	- 0.2
20	13.9	12.43	1.5	0
21	9.53	9.27	0.3	- 1.2
22	12.7	11.27	1.4	- 0.1
23	8.27	7.01	1.3	- 0.2
24	9.24	7.75	1.5	0
Average	10.78	9.41	1.4	0.1

*Not Averaged

PART II - B.O.D.

Lab #	River Water BOD mg/l	R.W. & Sample B BOD mg/l	Diff. Due to Sample B, BOD mg/l	Deviation mg/l
Theoretical			2.24	± 0.33
*SEC	2.24	4.22	1.98	- 0.26
1	1.2	3.0	1.8	- 0.44
2	3.34	4.88	1.54	- 0.70
3	6.0	8.1	2.1	- 0.14
4	-	-	-	-
5	1.6	4.0	2.4	+ 0.16
6	2.85	5.40	2.55	+ 0.31
7	1.01	2.18	1.17	- 1.07
8	.47	.74	0.27	- 1.97
9	1.7	4.1	2.4	+ 0.16
10	-	-	-	-
11	5.79	7.41	1.62	- 0.62
12	-	-	-	-
13	2.00	3.75	1.75	- 0.49
14	2.25	4.0	1.75	- 0.49
15	1.53	4.35	2.82	+ 0.58
16	3.15	5.3	2.15	- 0.09
17	0.15	1.57	1.42	- 0.82
18	2.8	4.8	2.0	- 0.24
19	0.43	2.4	1.97	- 0.27
20	1.0	2.4	1.4	- 0.84
21	2.3	4.3	2.0	- 0.24
22	1.6	2.7	1.1	- 1.14
23	3.03	3.65	0.62	- 1.62
24	3.17	4.60	1.43	- 0.81
Average	2.21	3.98	1.77	- 0.51

*Not Averaged

PART III - C.O.D.

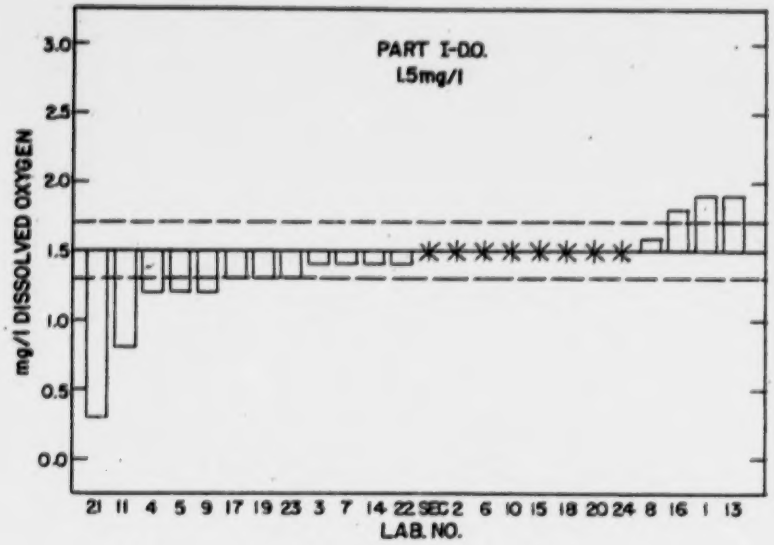
Lab #	River Water COD mg/l	R.W. & Sample B COD mg/l	Diff. Due to Sample B, COD mg/l	Deviation mg/l
Theoretical			21.3	± 3.2
*SEC	12.8	32.1	19.3	2.0
1	8.10	28.11	20.0	1.3
2	27.9	45.6	17.7	3.6
3	-	-	-	-
4	-	-	-	-
5	-	-	16.4	4.9
6	25.73	47.72	22.0	0.7
7	19.3	46.0	26.7	5.4
8	3.7	23.3	19.6	1.7
9	5.71	26.45	20.7	0.6
10	-	-	19.8	1.5
11	30.0	47.9	17.9	3.4
12	-	-	-	-
13	-	-	-	-
14	-	-	-	-
15	27.24	40.86	13.6	7.7
16	9.84	16.2	6.4	14.9
17	3.36	24.84	21.5	0.2
18	18.3	36.4	18.1	3.2
19	6.46	28.7	22.2	0.9
20	3.3	24.9	21.6	0.3
21	8.0	24.4	16.4	4.9
22	6.6	26.3	19.7	1.6
23	30.62	38.44	7.8	13.5
24	4.58	25.37	20.8	0.5
Average	14.4	32.7	18.3	3.0

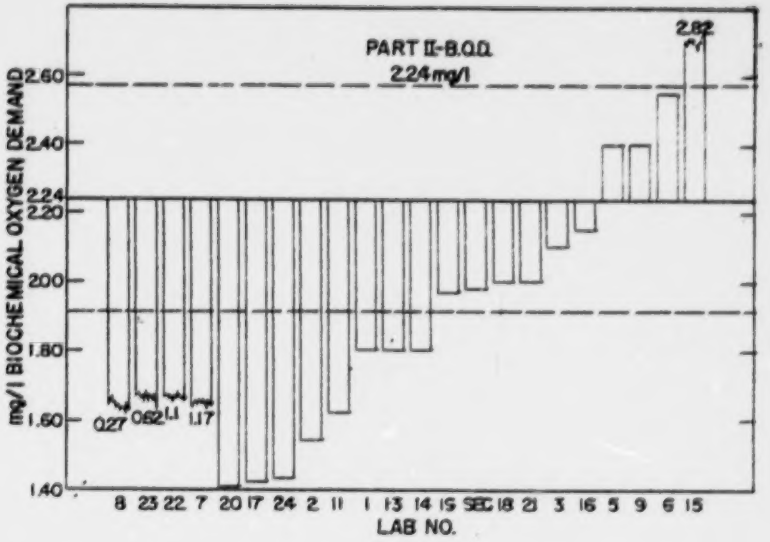
* Not Averaged

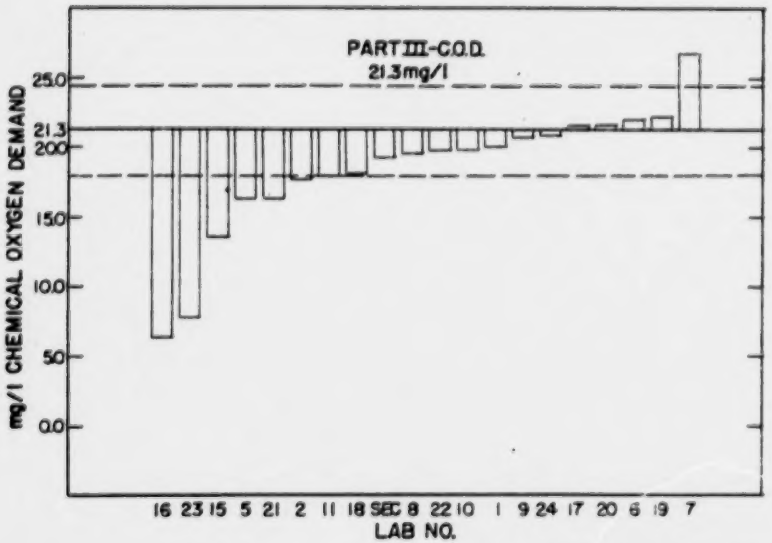
PART IV - NH_3-N

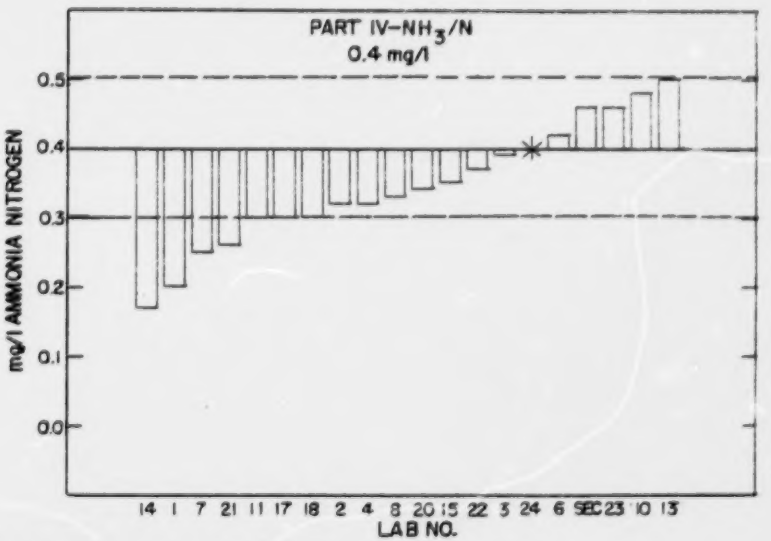
Lab #	River Water NH_3-N mg/l	R.W. & Sample C NH_3-N mg/l	Diff. Due to Sample C, NH_3-N mg/l	Deviation mg/l
Theoretical			0.40	± 0.10
*SEC	0.24	0.70	0.46	0.06
1	0.25	0.45	0.20	0.20
2	0.23	0.55	0.32	0.08
3	0.63	1.02	0.39	0.01
4	0.22	0.54	0.32	0.08
5	-	-	-	-
6	0.22	0.64	0.42	0.02
7	0.16	0.41	0.25	0.15
8	0.01	0.34	0.33	0.07
9	-	-	-	-
10	0.22	0.70	0.48	0.08
11	0.54	0.84	0.30	0.10
12	-	-	-	-
13	0.3	0.8	0.5	0.10
14	0.18	0.35	0.17	0.23
15	0.26	0.61	0.35	0.05
16	-	-	-	-
17	0.00	0.30	0.30	0.10
18	0.10	0.40	0.30	0.10
19	-	-	-	-
20	0.00	0.34	0.34	0.06
21	0.06	0.32	0.26	0.14
22	0.04	0.41	0.37	0.03
23	0.41	0.87	0.46	0.06
24	0.08	0.48	0.40	0.00
Average	0.21	0.55	0.34	0.06

*Not Averaged









ANALYTICAL REFERENCE SAMPLE TYPE II BD-1